

NOTE ON THE OCCURRENCE OF DAPHNIN IN THE ARTHROSOLEN.

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The *Arthrosolen polycephalus* or *Lasiosiphon polycephalus* (Nat. Ord. Thymeleaceae) is a perennial shrub which flowers in August and September. It is known to the farmers as the Januariesbosje, and in certain districts a decoction of the plant is reputed to be an efficacious remedy for lamziekte. On the other hand it has been included in the list of plants suspected of causing lamziekte (J. Burt-Davy, Preliminary Report on Botanical Investigation into Gal-Lamziekte, Union Agricultural Journal, August, 1912). As far as I can gather there is no reliable evidence either of its poisonous nature or of its medicinal virtues. The roots are extremely bitter to the taste.

As a few preliminary tests seemed to indicate the presence of an alkaloid, the roots and stems were extracted for several weeks with a cold 5 per cent. solution of acetic acid. After separating the roots and stems from the extract the latter was treated with lead acetate, and the supernatant liquid siphoned off from the precipitate. The extract was treated with sulphuretted hydrogen to remove the lead, and concentrated. The solution was then saturated with sodium chloride and repeatedly extracted with ether. On removal of the greater part of the solvent a yellowish substance separated out which was purified by repeatedly recrystallising from water with animal charcoal. In view of the sparing solubility of the compound in ether this method seemed unsatisfactory, but all attempts to improve it by substituting other solvents immiscible with water proved unsuccessful.

The compound was identified as daphnetin (3,4-dihydroxycoumarin). It melts at 253–256° (corr. 261°) with partial decomposition, but begins to darken at a much lower temperature. It is sparingly soluble in cold, but readily in hot water, with a yellow colour, separating out as a mass of interlaced acicular crystals of a slightly yellowish colour.

It is readily soluble in alcohol, glacial acetic acid, and ethyl acetate, sparingly so in ether, and insoluble in petroleum ether, benzene, chloroform, and carbon bisulphide.

The fact that it can be extracted from the aqueous-acetic acid solution by ether is due to the circumstance that the ethereal layer takes up some acetic acid, and that the daphnetin is more soluble in the mixture of ether and acetic acid than in pure ether.

Daphnetin crystallises from water with half a molecule of water, which is only expelled completely by heating to 120–130° for several hours.

0.2638 grm. lost 0.0115 H₂O. H₂O = 4.36 per cent.

I. 0.1594 grm. (anhydrous) gave 0.3556 CO₂ and 0.0523 H₂O.

II. 0.1210 grm. (anhydrous) gave 0.2708 CO₂ and 0.0352 H₂O.

I. C = 60.84 per cent. H = 3.65 per cent.

II. C = 61.04 per cent. H = 3.23 per cent.

C₉H₆O₄, $\frac{1}{2}$ H₂O requires H₂O = 4.81 per cent.

C₉H₆O₄ requires C = 60.67 per cent. H = 3.37 per cent.

The molecular weight was determined by the ebullioscopic method and by Barger's microscopic method.

I. 0.8137 grm. of substance in 23.92 grm. of alcohol gave Δt 0.24°. Molecular weight = 163.

II*. 0.0468 grm of substance in 15.54 c.c. of alcohol lie between 0.0002493 and 0.0002369 gram-molecules (using azo-benzene as standard), M.W. between 188 and 197.

C₉H₆O₄ has M.W. = 178.

The compound is soluble in sodium hydroxide with a yellowish-red colour. Aqueous or alcoholic solutions turn green on addition of ferric chloride. It strongly reduces Fehling's solution.

When the original aqueous-acetic acid extract had once been rendered alkaline, daphnetin could no longer be extracted, as it had undergone decomposition.

All the above properties are identical with those recorded for daphnetin.

The original acetic acid extract also contains glucose, which was identified by means of its osazone (m.p. 204°). After extraction the bitterness of the roots had entirely disappeared. The fact that both daphnetin and glucose (which are the products of the hydrolysis of the glucoside daphnin) were found in the extract seems fairly conclusive evidence that daphnin was originally present in the plant, and it is probable that it is the bitter principle of the roots.

By the method of extraction adopted the glucoside would naturally be hydrolysed.

It is interesting to note that the other plants previously recorded as containing daphnin, *Daphne Mezereum* and *Daphne alpina*, belong to the same order as the Arthrosolen.

The investigation is being continued.

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